

# FORMATION OF PARALLEL AQU/ORG TWO PHASE FLOW IN EXTENDED NANOCHANNEL BY PARTIAL MODIFICATION WITH MOLECULAR ABLATION USING EVANESCENT WAVE

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## ABSTRACT

We report a novel method for formation of pressure driven parallel two phase flow in extended nanochannel (10-1000 nm). A partial modification method by molecular ablation to spatially control the surface wettability in nanochannel was developed using the evanescent wave, which illuminates a region shorter than the optical wavelength. This method suggested a potential to form the parallel two phase flow by controlling an interface between water (aqueous phase) and dodecane (organic phase), which showed specific property of 3 times higher Laplace pressure at 500 nm channel compared to microchannels. The present study will contribute to develop nanofluidic systems using multi phase flows for chemical applications.

## KEYWORDS

Extended nanospace, two phase flow, pressure driven flow, surface modification.

## INTRODUCTION

Recent studies of extended nanospace have suggested potential of new engineering field of integrated chemical systems by revealing specific properties of liquid and chemical reaction [1]. In order to develop fluidic systems by extended nanochannels, a methodology of system engineering for integration of chemical processes is strongly required. Our group has developed a concept of integration using parallel multi-phase flows (immiscible liquids or gas/liquid) [2]. Unit of chemical process, e.g., mixing, reaction, separation, have been integrated by connecting in parallel and series. Although this method is considered to be applicable to extended nanospace, there are few methodologies to form parallel multi phase flow in nanochannel. Especially, partial surface modification method is strongly required to spatially control the surface wettability. Therefore we developed an optical method for partial modification for nanochannel to form the parallel two phase flow. In order to reveal interfacial properties in extended nanospace for precise surface control, two-phase flows in 500 nm-5000 nm channels were studied.

## EXPERIMENTAL SECTION

Figure 1 shows schematic of the partial modification method for two phase flow in nanochannel. Firstly, trimethylsilane (TMS) solution is injected into nanochannel to make hydrophilic glass channel walls hydrophobic. Then, the evanescent wave of 266 nm wavelength by total internal reflection of a pulse laser is illuminated toward a region within a side wall of the nanochannel of  $\sim 250$  nm to remove TMS by molecular ablation. Since the pattern of hydrophilic and hydrophobic region is formed by this partial ablation, an aqueous/organic two phase flow can be formed. The method was validated for flat fused-silica plate, and demonstrated for a 500 nm extended nanochannel.

Prior to the surface modification, two-phase flows in fused-silica channels formed by applying the external pressures were studied for various channel depths (500 nm, 1000 nm, 2000 nm, 5000 nm). Figure 2 shows schematics of (a) an experimental setup and (b) a two-phase flow channel. The extended-nano and microchannels were fabricated on a glass substrate by electron beam lithography and plasma etching. The aspect ratio (width/depth) of branch channel was one, while that of two-phase flow part of 100  $\mu\text{m}$  length was set to be two. Water and dodecane were used for aqueous and organic phases, respectively. In principle, parallel two-phase flow can be formed when the pressure difference between two fluids,  $\Delta P_f = P_{\text{org}} - P_{\text{aq}}$ , is equal to the Laplace pressure,  $P_L = 4\gamma\cos\theta/D$ , where  $P_{\text{org}}$  and  $P_{\text{aq}}$  is the fluidic pressure for organic and aqueous phase respectively,  $\gamma$  is the surface tension,  $\theta$  is the contact angle and  $D$  is the channel size, as shown in Figure 2(b). The applied pressures were varied for a range of 0–400 kPa to examine regime of two-phase flow (parallel flow or slug flow) and interfacial properties.

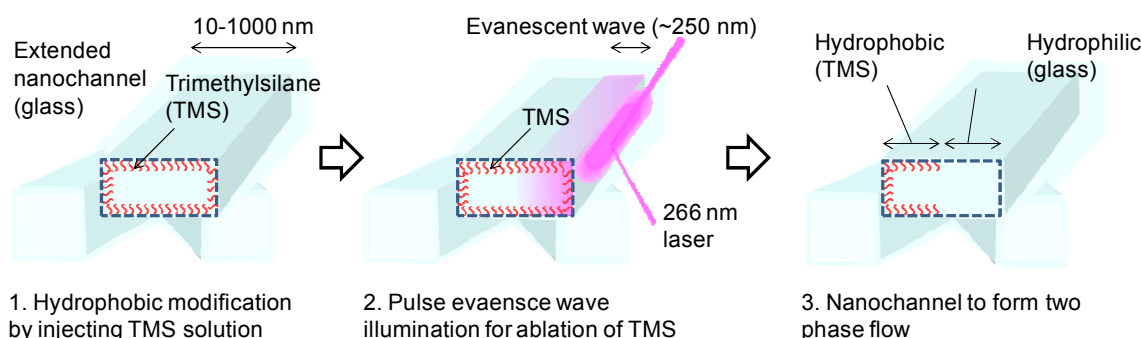


Figure 1. Schematic illustration of the partial modification method to spatially control the wettability in extended nanochannel using the molecular ablation using the evanescent wave.

## RESULTS AND DISCUSSION

Regime of two-phase flow in 500 nm-5000 nm fused-silica channels and interfacial properties were investigated. Figure 3 shows (a) two-phase flow in 2000 nm and 1000 nm channels observed by an optical microscope, and (b) regime of two-phase flow in 2000 nm channel as function of applied pressures. For microchannels, parallel two-phase flow was successfully formed for higher pressures over 100 kPa of high Capillary number ( $Ca = \mu U/\gamma$ , where  $\mu$  is the viscosity and  $U$  is the velocity), where the interface becomes stable by dominant viscous force, as shown in Figure 3(a) and (b). However, for extended nanochannels, parallel two-phase flow could not be formed for 0–400 kPa pressures, and became slug flow (Figure 3(a)). In order to evaluate properties of water-dodecane interface, the Laplace pressure at the interface was estimated from the injection pressure into the channel, as listed in Table 1. The experimental values of the Laplace pressure well agree with theoretical values for microspace, while the Laplace pressure in extended nanospace shows higher values than expected, 3 times higher for 500 nm channel. This higher Laplace pressure in extended nanospace is considered to be because of higher surface tension due to specific liquid structure predicted from our previous results for liquid confined in extended nanospace [1]. Considering the principle, the parallel two-phase flow becomes more unstable by the higher Laplace pressure, and results in slug flow. Therefore, it is concluded that a partial surface modification method is required to form parallel two-phase flow in extended nanochannel.

The proposed surface modification method was validated. TMS was modified on a fused-silica plate, and the evanescent wave of 266 nm wavelength was illuminated to remove TMS by ablation, by introducing a UV laser through the prism coupled with the glass plate. After the modification, Rhodamine B, which has strong affinity with TMS, was adsorbed on the surface, and then the surface modification was evaluated by fluorescent microscopy. Figure 4 shows (a) fluorescence image for Rhodamine B adsorbed on the surface after 60 min evanescent wave illumination, and (b) fluorescent intensity profile as function of time. A dark spot was observed in the fluorescent image, where TMS is removed and results in low adsorption of Rhodamine B. Temporal variation of the fluorescent intensity profile shows typical ablation process reported previously [3]. Results indicate that the modified TMS is removed by the ablation by the evanescent wave illumination.

Finally, the proposed modification method was demonstrated for a 500 nm channel (Figure 5). An optical alignment system to accurately illuminate the evanescent wave by observing the fluorescence was developed using an optical system and an EMCCD camera. The laser beam was converted to a laser sheet for the evanescent wave illumination toward the side channel wall. Result suggests that the two phase flow was partially formed in the nanochannel showing the water/dodecane interface. Although the accuracy of method is required to be improved, this study could prove availability of the partial surface modification method for formation of parallel two-phase flow in

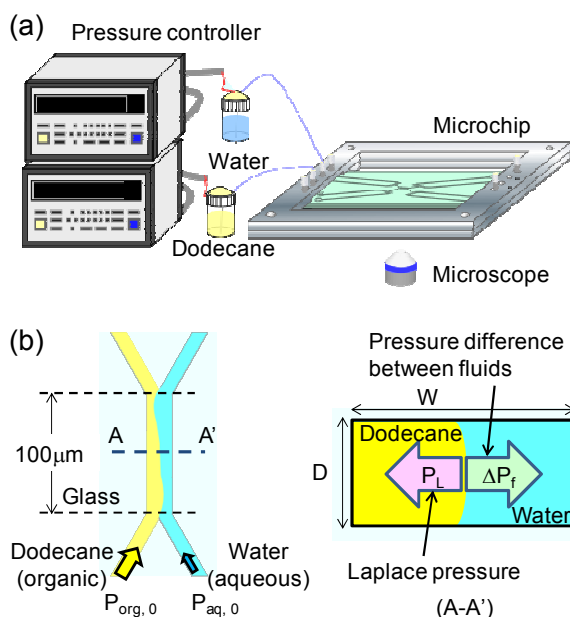


Figure 2. Schematics of (a) experimental setup and (b) two-phase flow channel of aspect ratio of two ( $W/D = 2$ ).

Table 1. The Laplace pressure at water-dodecane interface in fused-silica channels compared with theoretical value

Size (nm)	$P_L$ (exp.) [kPa]	$P_L$ (theory) [kPa]
5000	15.0	18.9
2000	40.0	47.4
1000	150	94.8
500	620	189

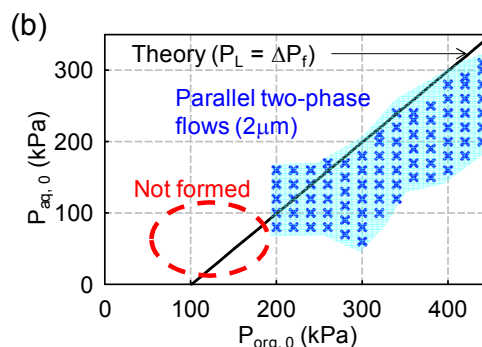
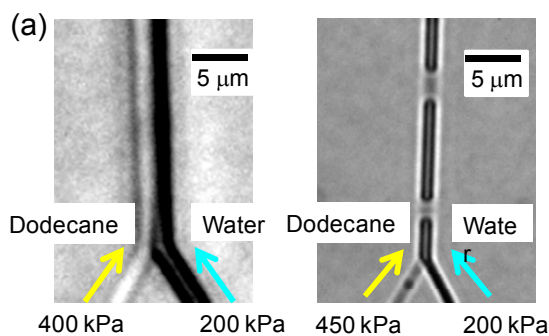


Figure 3. (a) two-phase flow in 2000 nm and 1000 nm channels observed by an optical microscope, and (b) regime of two-phase flow in 2000 nm channel as function of applied pressures.

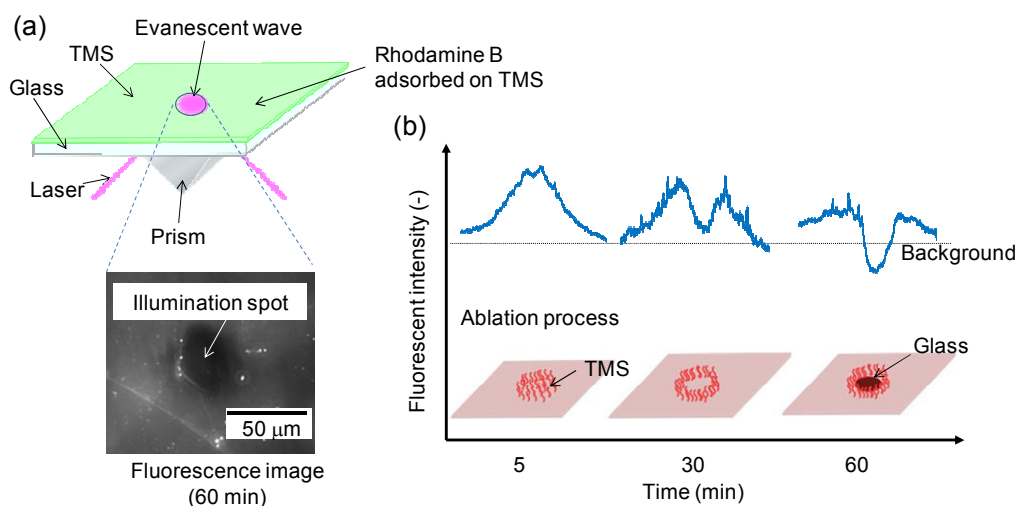


Figure 4. Validation of the molecular ablation by the evanescent wave by the fluorescence detection. Rhodamine B was adsorbed on TMS modified on the glass surface. The fluorescence image shows a dark spot where TMS is removed.

extended nanochannel.

## CONCLUSIONS

A method to form parallel two-phase flow in extended nanochannel was studied. An optical partial modification method by using molecular ablation by evanescent wave was proposed. Investigation of regime of two-phase flow in fused silica channel revealed that parallel two-phase flow can be formed in microspace, while two-phase flow in extended nanospace becomes slug flow in a pressure range of 100-400 kPa. The results indicated that the Laplace pressure of water-dodecane interface becomes higher than theoretical value in extended nanospace, probably due to specific liquid structure predicted by our previous study. This suggests that the partial surface control is required to form parallel two-phase flow in extended nanochannel. The demonstration of the partial modification method for 500 nm channel suggested possibility of formation of two-phase flow in extended nanochannel. This method will greatly contribute to nanofluidics for integration of chemical unit operations into extended nanospace by using continuous multi-phase flows.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1] T. Tsukahara, K. Mawatari and T. Kitamori, *Integrated Extended-nano Chemical Systems on a Chip*, Chem. Soc. Rev., 39, pp. 1000-1013, (2010).
- [2] M. Tokeshi, T. Minagawa, K. Uchiyama, A. Hibara, K. Sato, H. Hisamoto and T. Kitamori, *Continuous Flow Chemical Processing on a Microchip by Combining Micro Unit Operations and a Multiphase Flow Network*, Anal. Chem., 74, pp. 1565-1571, (2002).
- [3] N. Hartmann, S. Franzka, J. Koch, A. Ostendorfer and B. N. Chichkov, *Subwavelength Patterning of Alkylsiloxane Monolayers via Nonlinear Processing with Single Femtosecond Laser Pulses*, Appl. Phys. Lett., 92, 223111, (2008).

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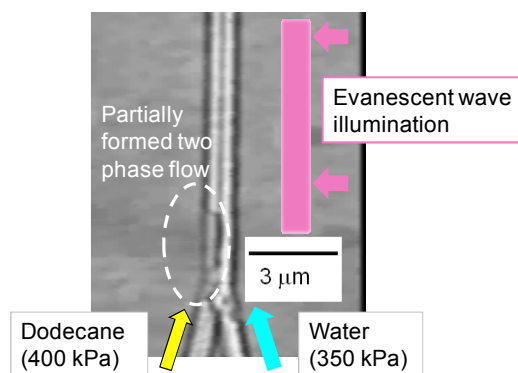


Figure 5. Results of formation of two phase flow in 1000 nm width and 500 nm depth extended nanochannel by the partial modification. The two phase flow was partially formed near the junction.